

# A Novel Approach Towards PGM-free PEM Fuel Cell Cathodes

C. Anson<sup>1</sup>, J. Gerken, Y. Preger, S. Biswas, T. Root, S. Stahl<sup>2</sup>

University of Wisconsin, Madison, WI, USA

<sup>1</sup>canson@wisc.edu, <sup>2</sup>stahl@chem.wisc.edu

## ABSTRACT

One of the major obstacles preventing widespread implementation of PEM fuel cells is the requirement for prohibitive loadings of Pt at the cathode to achieve high activity for the oxygen reduction reaction. To address this concern, we are developing a novel PEM fuel cell, where the oxygen reduction reaction is spatially separated from the electrode. In our chemically regenerable redox cathode, a soluble organic redox mediator undergoes facile reduction at the cathode and transports electrons and protons through solution to a non-PGM catalyst, where the aerobic oxidation of the mediator (and therefore, reduction of O<sub>2</sub>) occurs. The oxidized mediator can then return to the electrode, where it is again reduced. The use of non-PGM catalysts in our system does not have the same drawbacks as in conventional PEM fuel cells, and the high performance possible with this approach could lead to an activity- and cost-competitive design relative to conventional PEMFCs.

**Keywords:** mediated fuel cells, flow cathode, non-PGM, hydrogen

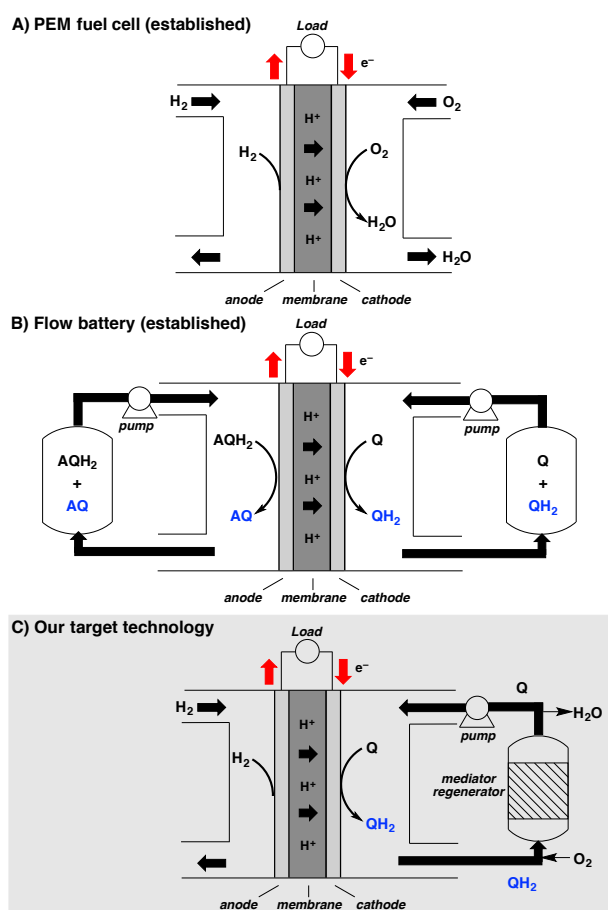
## 1 INTRODUCTION

Electrochemical energy generation and storage will play an increasingly important role in society's energy needs as we move towards higher utilization of renewable energy sources integrated with the grid. Fuel cells will be an important component of the expanding portfolio of these electrochemical energy applications, due to their advantages in efficiency and environmental benefits over combustion-based power and electricity generation. The largest class of fuel cell technology are proton-exchange membrane fuel cells (PEMFCs) [1]. While decades of research have led to important progress in PEMFCs, and fuel cell technology in general, their widespread adoption in the marketplace continues to be constrained by accessible power densities, durability, and device economics. A key limitation of PEMFC technology is the cathode chemistry, where oxygen (O<sub>2</sub>) is reduced, due in part to the complicated 3-phase reactivity that must be managed at the cathode. To sufficiently catalyze this reaction, high loadings of expensive platinum catalysts are typically used. The cost associated with the Pt catalyst have been forecast to contribute over 40% of the PEM stack cost in automotive applications [2]. In addition, electrode and membrane durability issues are present at the cathode, typically due to

the formation of reactive oxygen-based radical species and the degradation under the high-potential conditions present at start-up and shutdown. To address these concerns, we have drawn inspiration from the field of redox flow batteries and developed a flow cathode, where O<sub>2</sub> reduction is moved off-electrode. Our approach has the potential to achieve higher performance at lower system costs than conventional PEMFCs.

PEMFCs directly produce electricity by the oxidation of a fuel (typically H<sub>2</sub> gas or a MeOH solution) at the anode and reduction of gaseous O<sub>2</sub> at the cathode. The anode and cathode are separated by a proton-selective membrane, and electrons are transported through an external circuit to generate electricity (Figure 1A). As discussed above, high loadings of expensive Pt are typically required to catalyze O<sub>2</sub> reduction at the cathode at reasonable rates and potentials. Non-platinum catalysts composed of iron or cobalt species on nitrogen-doped carbon [3] have shown some promise in low-power applications, and the first commercial system was recently released [4]. However, higher performance catalysts will be needed to displace platinum in most cases. A major limitation of non-platinum catalysts is the increased cell resistance from the increased electrode thickness required to offset the lower activity of these catalysts. Reports on automotive PEMFC applications suggest that with current non-platinum catalysts, any price decrease gained by removal of platinum is typically more than offset by the increased stack infrastructure required [5].

In contrast, redox flow batteries operate by using soluble, redox-active mediators to store and retrieve electrical energy. These mediators are stored in external tanks and are flowed past the electrodes during charge/discharge. During discharge, a low-potential mediator is oxidized at the anode and a high-potential mediator is reduced at the cathode (Figure 1B). In this example, the low potential mediator is represented by the anthraquinone (AQ)/anthrahydroquinone (AQH<sub>2</sub>) redox couple, and the high-potential mediator is represented by the quinone (Q)/hydroquinone (QH<sub>2</sub>) redox couple. To charge the battery, these operations are reversed by applying current from an external source. Historically, inorganic species such as vanadium, iron, chromium, bromine, or zinc have been utilized as mediators. Currently commercialized technology includes V/V, Fe/Cr, Fe/Fe, Zn/Fe, and Zn/Br<sub>2</sub>. Recent work has focused on the use of organic materials, such as quinones (as indicated in Figure 1B) [6]. Organic materials are more modular than inorganic mediators, as their redox potential, solubility and redox



**Figure 1.** Schematic drawing of A) PEM fuel cell, B) redox flow battery in discharge mode, and C) Our proposed fuel cell system.

kinetics can be readily adjusted by varying the substitution pattern. Furthermore, organic mediators can potentially be sourced from renewable materials. The two-phase interaction between the dissolved mediator and the electrode has significant advantages over the three-phase process involved in PEMFCs, leading to much better electrode performances.

Our patented fuel cell strategy [7] draws inspiration from flow battery applications and employs a dissolved quinone mediator, **Q**, that undergoes efficient reduction at the cathode. The reduced mediator, **QH<sub>2</sub>**, is passed through a "mediator regenerator", which contains a heterogeneous catalyst capable of aerobically oxidizing the reduced mediator (Figure 1C). During the aerobic oxidation, O<sub>2</sub> is reduced to H<sub>2</sub>O. The oxidized mediator is then pumped back to the electrode, where it again can undergo electrochemical reduction. In our design, the anode is the same as in a conventional PEMFC, where H<sub>2</sub> gas is oxidized at a Pt/C catalyst. This "chemically regenerable redox fuel cell" (CRRFC) design provides a means to achieve high cathodic current densities because the organic mediator may be designed with high solubility in the electrolyte and rapid electrode kinetics. The electrode and

membrane can be optimized for liquid flow versus the challenging 3-phase reactivity in conventional PEMFCs. Instead, the difficult O<sub>2</sub> reduction reaction can be optimized in the mediator regenerator using well-developed flow chemistry techniques without regard for the electrochemical or mass-transport limitations associated with traditional fuel cells. A preliminary techno-economic analysis of our approach suggests that our system can be competitive with conventional PEMFC technology.

## 2 CHEMICALLY REGENERABLE REDOX FUEL CELLS

CRRFCs have been investigated for many decades [8], with representative mediators including bromine, vanadium, and iron. However, these systems have suffered from one or more undesirable characteristics, such as high mediator molecular weight, low molecular solubility, low mediator reduction potential, slow aerobic oxidation, and/or mediator or catalyst volatility. For example, the first report of a CRRFC cathode was by Posner in 1955, using a Br<sub>2</sub> mediator and NO<sub>x</sub>-based catalyst [9]. In this case, while Br<sub>2</sub> and NO<sub>x</sub> are capable of operating at high redox potentials, their volatility limits long term practicality. Other important examples of cathodic CRRFC chemistry includes the VO<sup>2+</sup>/VO<sub>2</sub><sup>+</sup> mediator paired with NO<sub>x</sub> or Pt-based catalysts [10] and HNO<sub>3</sub>-mediated cathodes developed at the Esso Research and Engineering Company in the 1960's [11]. The most advanced efforts have focused on the use of vanadium-containing polyoxometalates (POMs) as combined catalysts/mediators. Originally reported by workers from Ford in the 1980's [12], this system was more recently commercialized by Acal Energy Ltd. in the UK [13]. In 2012, a 3 kW device was installed as a back-up power source at a chemical plant in the UK [14]. Fundamental studies on the system, reported by Davies and coworkers [15], indicate that high power densities (> 1 W/cm<sup>2</sup>) can be transiently obtained using POMs, but the steady-state performance is much lower and limited by slow reoxidation by O<sub>2</sub>. While the CRRFC strategy has the potential for substantial positive impacts on fuel cell technology, the previously reported systems have not been able to achieve this potential. Our novel approach addresses the problems with previous reports.

## 3 OUR APPROACH

As discussed above, our approach utilizes *organic* mediators paired with a *heterogeneous* catalyst to mediate O<sub>2</sub> reduction in the cathode of a chemically regenerable redox fuel cell. This approach allows us to overcome the challenges present for previously reported mediated fuel cell technologies. For example, neither the catalyst nor the mediator are volatile, the mediator can be designed to have high solubility, and the mediator and catalyst can be optimized independently of each other to ensure facile

aerobic oxidation. This project has been developed in three parallel pathways:

- 1) Mediator development
- 2) Catalyst development
- 3) Integration, fuel cell testing and modeling

Mediator development has focused on the design and synthesis of stable, high-potential, soluble quinones. A major benefit of our approach is the tunability of organic mediators. While metal redox couples, such as  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{VO}^{2+}/\text{VO}_2^+$ , have relatively immutable redox potentials, the redox potential of an organic species can be tuned by varying the substituents on it. For example, Aspuru-Guzik and coworkers computationally studied the redox potentials and solubilities of a wide range of quinones, and found their redox can vary by over 2.4 V, with numerous examples of soluble quinone mediators with redox potentials of over 1.0 V vs. NHE [16]. However, quinones undergo various decomposition pathways under acidic aqueous conditions [6e], and we are currently working on identifying strategies to mitigate these decomposition pathways, which include hydroxylation by water, which lowers the redox potential, and oligomerization/polymerization, which leads to insoluble products. In addition to targeting high potentials and good stability, an efficient, inexpensive synthesis of these mediators needs to be identified, to ensure that the CRRFC device is economically viable.

Catalyst development has focused on identifying heterogeneous catalysts that display stability under the acidic aqueous conditions used in our fuel cell. Due to the off-electrode location of the catalyst, there are not the same constraints on proton- and electron-conductivity that exist for conventional on-electrode catalysts. This difference means that the increased resistance issues with non-PGM catalysts *on-electrode* will no longer be a constraint on performance. For this reason, new supports, such as silica, could be advantageous in the mediator regenerator. Catalysts of interest are first tested on a small scale in the aerobic oxidation of a typical redox mediator, and promising catalysts can be implemented in a flow reactor. At this point, important parameters, such as particle size, reactor size, and liquid/gas flow rates can be optimized. These metrics will be important in preventing large pumping losses while ensuring high catalytic rates.

Once stable mediators and catalysts are identified, the complete fuel cell system can be assembled. This system includes the fuel cell MEA, the mediator regenerator, and other required components, such as pumps. Once assembled, polarization and time-on-stream experiments can be conducted, which probe the overall performance of the system. Based on preliminary performance data, we have developed a basic model that is able to account for activation, ohmic, and mass-transport losses. This model allows for extrapolation of higher performing mediators and catalysts. These forecast performance metrics can be implemented into a preliminary technoeconomic analysis, based on reported data for fuel cells [2,4] and flow batteries

[17]. Based on estimates for fuel cell stack costs and our own calculations, our fuel cell design can outcompete conventional PEMFCs on a price-basis at a variety of mediator redox potentials ( $> 0.8$  V), and can have higher power density metrics with a mediator redox potential of 1.1 V.

## 4 CONCLUSIONS

We have described our novel approach towards PEMFCs, utilizing a flow-based cathode that will enable enhanced integration of non-PGM catalysts paired with an organic quinone mediator. Development of higher-performance mediators and catalysts is on-going. Based on preliminary fuel cell performance, we estimate that our mediated cathode approach will be lower cost than conventional, Pt-containing PEMFCs. We are in the beginning stages of commercializing this technology and are exploring the best market fit for this technology.

## 5 REFERENCES

- [1] E4tech, "The Fuel Cell Industry Review – 2017" <http://www.fuelcellindustryreview.com>, accessed 2/13/18.
- [2] (a) James, B. D.; Huya-Kouadio, J. M.; Houchins, C.; DeSantis, D. A. "Mass Production Cost Estimation of Direct  $\text{H}_2$  PEM Fuel Cell Systems for Transportation Applications: 2016 Update" Prepared for DOE by Strategic Analysis, September 2016. (b) Wilson, A.; Kleen, G.; Papageorgopoulos, D. "Fuel Cell System Cost – 2017", DOE Hydrogen and Fuel Cells Program Record #17007, September 30, 2017.
- [3] Gewirth, A. A.; Varnell, J. A.; DiAscro, A. M. "Nonprecious Metal Catalysts for Oxygen Reduction in Heterogeneous Aqueous Systems." *Chem. Rev.* **2018**, DOI: 10.1021/acs.chemrev.7b00335.
- [4] "Ballard to Offer World's First PEM Fuel Cell Product Using Non Precious Metal Catalyst", September 12, 2017, <http://ballard.com/about-ballard/newsroom/news-releases/2017/09/13/ballard-to-offer-world-s-first-pem-fuel-cell-product-using-non-precious-metal-catalyst>
- [5] Zelenay, P. "State of the Art of PGM-free Catalyst Activity and Durability" Presented at ElectroCat Workshop, Argonne National Lab, July 26 2016.
- [6] For a review discussing the evolution of flow batteries utilizing organic mediators, see: (a) Winsberg, J.; Hagemann, T.; Janoschka, T.; Hager, M. D.; Schubert, U. S. "Redox-Flow Batteries: From Metals to Organic Redox-Active Materials." *Angew. Chem. Int. Ed.* **2017**, *56*, 686-711. For examples of quinones used in the cathode of flow batteries, see: (b) Huskinson, B.; Nawar, S.;

- Gerhardt, M. R.; Aziz, M. "Novel Quinone-Based Couples for Flow Batteries" *ECS Trans.* **2013**, *53*, 101 - 105; (c) Yang, B.; Hooper-Burkhardt, L.; Wang, F.; Surya Prakash, G. K.; Narayanan, S. R. "An Inexpensive Aqueous Flow Battery for Large-Scale Electrical Energy Storage Based on Water-Soluble Organic Redox Couples" *J. Electrochem. Soc.* **2014**, *161*, A1371 - A1380; (d) Yang, B.; Hooper-Burkhardt, L.; Krishnamoorthy S.; Murali, A.; Prakash, G. K. S.; Narayanan, S. R. "High-Performance Aqueous Organic Flow Battery with Quinone-Based Redox Couples at Both Electrodes." *J. Electrochem. Soc.* **2016**, *163*, A1442-A1449. (e) Hooper-Burkhardt, L.; Krishnamoorthy, S.; Yang, B.; Murali, A.; Nirmalchandar, A.; Prakash, G. K. S.; Narayanan, S. R. "A New Michael-Reaction Resistant Benzoquinone for Aqueous Organic Redox Flow Batteries." *J. Electrochem. Soc.* **2017**, *164*, A600-A607.
- [7] Stahl, S. S.; Gerken, J. B.; Anson, C. W. "Charge Transfer Mediated-based Systems for Electrocatalytic Oxygen Reduction", U.S. Patent 9,812,727. Nov. 7, 2017.
- [8] Tolmachev, Y. V.; Vorotyntsev, M. A. "Fuel Cells with Chemically Regenerative Redox Cathodes (Review)." *Russ. J. Electrochem.* **2014**, *50*, 403-411.
- [9] Posner, A. M. "Redox Fuel Cell." *Fuel*, **1955**, *34*, 330-338.
- [10] (a) Folkesson, B. Chemically regenerative redox fuel cells II. Regeneration reaction studies. *J. Appl. Electrochem.* **1990**, *20*, 907-911. (b) Bergens, S. H.; Gorman, C. B.; Palmore, G. T. R.; Whitesides, G. M. A Redox Fuel Cell That Operates with Methane as Fuel at 120 °C. *Science*, **1994**, *265*, 1418-1420. (c) Larsson, R.; Folkesson, B. Method for Producing Electric Energy in a Biofuel-Powered Fuel Cell. U.S. Patent 5660940, 1997.
- [11] Shropshire, J. A.; Tarmy, B. L. The Nitric Acid-Oxygen Redox Electrode in Acid Electrolyte. *Adv. Chem.* **1969**, *47*, 153-165.
- [12] (a) Oei, D-G. "Chemically regenerative redox fuel cells." *J. Applied. Electrochem.* **1982**, *12*, 41-51. (b) Kummer, J. T.; Oei, D-G. "A chemically regenerative redox fuel cell." *J. Applied Electrochem.* **1982**, *12*, 87-100. (c) Kummer, J. T.; Oei, D-G. "Chemically Regenerable Redox Fuel Cell and Method of Operating the Same." US Patent 4,396,687, August 2, 1983.
- [13] Creeth, A. "Pt-free PEM cathode technology with fundamental durability benefits: FlowCath" *Fuel Cells Bulletin*, **2011**, *2011*, 12-15.
- [14] "ACAL Energy's FlowCath® Handover Day: Solvay Interox site, Warrington, UK." FuelCellToday, <http://www.fuelcelltoday.com/analysis/event-reports/2012/acal-energy's-flowcath-handover-day>.
- [15] (a) Gunn, N. L. O.; Ward, D. B.; Menelaou, C.; Herbert, M. A.; Davies, T. J. "Investigation of a chemically regenerative redox cathode polymer electrolyte fuel cell using a phosphomolybdovanadate polyoxoanion catholyte." *J. Power Sources*, **2017**, *348*, 107-117. (b) Ward, D. B.; Gunn, N. L. O.; Uwigena, N.; Davies, T. J. "Performance comparison of protonic and sodium phosphomolybdovanadate polyoxoanion catholytes within a chemically regenerative redox cathode polymer electrolyte fuel cell" *J. Power Sources*, **2018**, *375*, 68-76.
- [16] Er, S.; Suh, C.; Marshak, M. P.; Aspuru-Guzik, A. "Computational design of molecules for an all-quinone redox flow battery." *Chem. Sci.* **2015**, *6*, 885-893.
- [17] Darling, R. M.; Gallagher, K. G.; Kowalski, J. A.; Ha, S.; Brushett, F. R. "Pathways to low-cost electrochemical energy storage: a comparison of aqueous and nonaqueous flow batteries." *Energy Environ. Sci.* **2014**, *7*, 3459-3477.